PB89-120760

Octanol/Water Partition Coefficients for Evaluation of Hazardous Waste Land Disposal: Selected Chemicals

(U.S.) Environmental Research Lab., Athens, GA

Aug 88

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO.	2.	3. PB89-120760
EPA/600/M-88/010		

4. TITLE AND SUBTITLE
OCTANOL/WATER PARTITION COEFFICIENTS FOR EVALUATION OF HAZARDOUS WASTE LAND DISPOSAL: Selected Chemicals

5. REPORT DATE
August 1988

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. Jackson Ellington and Frank E. Stancil, Jr.

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens GA 30613

10. PROGRAM ELEMENT NO.
ABWD1A

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory - Athens, GA
Office of Research and Development
U.S. Environmental Protection Agency
Athens GA 30613

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/01

15. SUPPLEMENTARY NOTES
ENVIRONMENTAL RESEARCH BRIEF

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	5
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	A02 $10.95

EPA Form 2220-1 (Rev. 4-77) PREVIOI

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United States
Environmental Protection
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Environmental
Research Laboratory
Athens, GA 30613

Research and Development EPA/600/M-88/010 August 1988

EPA

ENVIRONMENTAL RESEARCH BRIEF

Octanol/Water Partition Coefficients for Evaluation of Hazardous Waste Land Disposal: Selected Chemicals

J.Jackson Ellington and Frank E. Stancil, Jr.

Abstract

Octanol/water partition coefficients were extracted from the literature, calculated using a molecular fragment data base (CLOGP), or measured in the laboratory for selected chemicals. Agreement between measured values and calculated values was good for chemicals for which both types of information was available. Partition coefficients are reported for members of six chemical classes: polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, phosphate esters, nitrogen mustards, alkylamines, and amines. Measurements of the octanol/water partition coefficients of two standard reference chemicals, pyrene (log $K_{ow} = 5.05 \pm 0.27$) and biphenyl (log $K_{ow} = 4.09 \pm 0.12$), were interspersed with determinations of log K_{ow} of compounds of interest to serve as quality assurance indicators.

Background

The Hazardous and Solid Waste Amendments of 1984 to the Resource Conservation and Recovery Act (PL 98-616) stipulate that land disposal of "hazardous wastes" is prohibited unless the EPA Administrator determines that specific compounds are not likely to reach unacceptable levels in ground water at an individual disposal site. The amendments define hazardous waste as any of 362 specific compounds (either part of or inclusive of Appendix VIII compounds). In compiling this list, major considerations were toxicity of the material and quantity of waste material generated annually.

To provide a practical tool for determining which listed hazardous materials may be accepted for land disposal and under what conditions, a relatively simple model that would estimate potential ground-water contamination for each listed chemical at a specified withdrawal point downgradiant from a failed facility was developed. The model calculates horizontal chemical movement in the aquifer based on advection, dispersion, sorption, and transformation.

To implement this modeling approach, it was necessary to acquire octanol/water partition coefficients for each of the 362 chemicals identified by the U.S. Environmental Protection Agency's Office of Solid Waste. The octanol/water partition coefficients are used to estimate sorption equilibrium constants (k_d). Karickhoff and Ellington et al. reported log K_{ow} values for 251 and 40 chemicals, respectively. This report presents the octanol/water partition data developed by Ellington and coworkers along with values for an additional six chemicals. Included are members of six chemical classes: polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, phosphate esters, nitrogen mustards, alkylamines, and amides. Because of the procedures followed in their development, the K_{ow} data may be used with confidence in any appropriate modeling application.

Each chemical was evaluated with regard to applicability of a sorption estimation protocol. Where applicable, K_{ow} values were obtained from a data base compiled by Veith[1]. The K_{ow} values in Veith's data base were obtained from Medchem Software Release 3-33, a data base developed by Leo and Weininger[2]. Medchem Software Release 3-33 contains STARLIST, a data base of measured log K_{ow} values[3], and CLOGP, a data base that contains values for molecular fragments that allow calculation of a log K_{ow}.

Laboratory Procedures

The method of Karickhoff et al.[4] was used at the Environmental Research Laboratory, Athens GA (ERL-Athens) to determine the log K_{ow} values. Reagent grade

The authors are with the U.S. Environmental Protection Agency's Environmental Research Laboratory, Athens, GA 30613

octanol was extracted once with 0.1 *N* sodium hydroxide, and twice with distilled water. It was subsequently distilled at atmospheric pressure. The first 15 ml of distillate were discarded, then approximately 70% of the remaining volume was collected and stored in an amber bottle. Mutually presaturated water (deionized, organic free) and octanol were used in the experiments.

Log K_{ow} Greater than 1000

Those chemicals for which the K_{ow} was expected to be greater than 1000 were dissolved in octanol, and 2 ml of this solution was added to 40 ml of octanol-saturated water contained in 50-ml stainless steel centrifuge tubes. The tubes were sealed and gently mixed by hand-swirling for 15 minutes. After standing for a minimum of 12 hours, the tubes were centrifuged for 30 min at 15,000 rpm (Sorvall SS-34) and the phases sampled directly from the centrifuge tubes. To perform the analysis, an aliquot of octanol (0.25 - 1.0 ml) was removed from the centrifuge tube and added either directly into an analysis cell (UV) or a diluting solvent suitable for subsequent analysis by gas chromatography (GC) or high performance liquid chromatography (HPLC). The remaining octanol and top 1 ml of water were removed from the tube and discarded before withdrawing an aliquot of the water layer for analysis. Care was taken to avoid touching the inner wall of the tube. If the aqueous layer had been contaminated with even a trace of the octanol containing the test chemical, significant error in K_{ow} measurement could have resulted.

For analysis by GC, the aqueous phase was extracted with three 2-ml portions of hexane. The hexane extract was concentrated to 1 ml by nitrogen blowdown before addition of an internal standard and subsequent quantitation by GC. After establishing GC detector response for the hexane extract of the aqueous layer, the octanol aliquot was serially diluted with hexane until detector response for the analysis of the octanol dilution and hexane extract were within a factor of two. An internal standard then was added to the octanol dilution before quantitation by GC. The internal standard allowed normalization of the amounts of chemical in each layer, and when combined with the dilution and concentration factors in equation 1, permitted calculation of the K_{ow}.

$$K_{ow} = \frac{[OR][DCF]}{[WR][DCF]} \qquad (1)$$

where:

OR = Value obtained from octanol layer
WR = Value obtained from water layer
DCF = Dilution or concentration factor

If the chemical is intractable to analysis by GC, alternative analytical methods (UV, HPLC, etc.) must be established to allow calculation of the ratio expressed in equation 1.

Log K_{ow} Less Than 1000

Measurement of K_{ow}s for chemicals having expected values less than 1000 is illustrated by the following example. Lasiocarpine was dissolved in 5 ml of octanol and added to 5 ml of water. After gentle mixing, standing, and centrifugation, aliquots from each phase were diluted with CH_3CN and subsequently analyzed by HPLC. The two compounds having high water solubility, [azaserine and ethylene-*bis* (dithiocarbamic acid)], were dissolved in water rather than octanol. The partition equilibrium was established using equal volumes of stock solution water and octanol. Concentrations in the water and octanol were determined by appropriate HPLC and UV methods, respectively. Partition coefficients were calculated using equation 1 and the response values and dilution or concentration factors obtained for the octanol and water phases.

Results and Discussion

Table 1 contains the list of chemicals and corresponding log K_{ow} values from Ellington et al. plus recently measured values for six more compounds. The log K_{ow} value for each chemical was either measured at ERL-Athens, obtained from literature sources, or calculated using CLOGP. The higher ERL-Athens values for pronamide and lasiocarpine (Table 2) may reflect the difficulty in obtaining CLOGP calculations for polyfunctional compounds. Many literature K_{ow}s were given as single measurements. For two chemicals, literature values varied over two orders of magnitude (chlordane and toxaphene). The ERL-Athens values for diallate and kepone showed the greatest deviation from literature values. Generally, the CLOGP-calculated values were in good agreement with measured values except as noted previously for pronamide and lasiocarpine.

Ionizable compounds listed in Table 1 are present in aqueous solution as both ionized and unionized species. The pK_a or pK_b of such ionizable compounds as well as the pH and ionic strength of the aqueous systems must be known when using their respective K_{ow}s to predict sorption[14].

Measurement of the K_{ow}s for pyrene and biphenyl was interspersed with measurement of the K_{ow}s of the other chemicals. Reproduction of the K_{ow}s of these standard reference compounds (SRCs) ensured that the experimental conditions were of known precision and helped in evaluating the accuracy and precision of measurements for other compounds.

Acknowledgments

A note of appreciation to Dr. Gilman Veith (Environmental Research Laboratory, USEPA, Duluth, MN) for providing the STARLIST and CLOGP values, and Drs. William Steen and Chad Jafvert (ERL-Athens) for reviewing the manuscript.

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Table 1. Compilation of Log K_{ow} Values for Appendix VIII Chemicals

CAS No.	Chemical	Log K_{ow}	Source
309-00-2	Aldrin	5.11 ± 0.04[a] (n = 4)	d
115-02-6	Azaserine	-2.00 ± 0.06[b] (n = 4)	d
56-55-3	Bena(a)anthracene	5.66	e
205-99-2	Benzo(b)fluoranthene	6.12	e
225-51-4	Benz(c)acridine	4.61	e
305-03-3	Chlorambucil[c]	3.61	e
57-74-9	Chlordane (Tech)	5.54	e
494-03-1	Chlornaphthazine[c]	4.53	e
50-18-0	Cyclophosphamide[c]	0.63	f
72-54-8	DDD (p,p'isomer)	6.02	f
2303-16-4	Diallate	4.49 ± 0.06 (n = 4)	d

(Continued)

Table 1. (Continued)

CAS No.	Chemical	Log K_{ow}	Source
189-55-9	1,2,7,8-Dibenzopyrene	6.94	e
60-57-1	Dieldrin	4.09 ± 0.07 (n = 2)	d
1615-80-1	N,N'-Diethylhydrazine	-0.30	e
311-45-5	Diethyl-*p*-nitrophenyl phosphate	1.98	f
3288-58-2	0,0 Diethyl-S-methyl-dithiophosphate	2.79	e
124-40-3	Dimethylamine	-0.49	e
540-73-8	1,2-Dimethylhydrazine	-1.36	e
131-89-5	4,6-Di-Nitro-0-cyclohexyl phenol	4.12 ± 0.04 (n = 4)	d
298-04-4	Disulfoton	3.94 ± 0.05 (n = 5)	d
115-29-79	Thiodan (Endosulfan II measured)	4.52 ± 0.10 (n = 3)	d
72-20-8	Endrin	4.92 ± 0.18 (n = 4)	d
111-54-6	Ethylene-*bis*(dithiocarbamic acid) as disodium salt	-2.70 ± 0.07 (n = 3)	d
62-74-8	Fluoroacetic acid, sodium salt	-0.06	e
50-00-0	Formaldehyde	0.35	f
765-34-4	Glycidylaldehyde	-1.05	e
76-44-8	Heptachlor	5.53 ± 0.22 (n = 4)	d
757-58-4	Hexaethyl-tetraphosphate	5.25	e
143-50-4	Kepone	5.30 ± 0.09 (n = 4)	d
303-34-4	Lasiocarpine	1.28 ± 0.14 (n = 4)	d
148-82-3	Melphalan[c]	-0.21	e
91-80-5	Methapyrilene	2.74	e
16752-77-5	Methomyl	0.60	f
72-43-5	Methoxychlor	4.68	f
298-00-0	Methyl parathion	2.86	f
4549-40-0	*N*-Nitroso-methylvinylamine	0.003	e
56-38-2	Parathion	3.83	f
298-02-2	Phorate	2.92	f
23950-58-5	Pronamide	3.43 ± 0.10 (n = 4)	d
18883-66-4	Streptozocin	-1.45	e
3689-24-5	0,0,0,0-Tetraethyl dithiopyrophosphate	3.83 ± 0.10 (n = 4)	d
8001-35-2	Toxaphene	4.63 ± 0.33 (n = 4)	d
12002-48-1	1,2,4-Trichlorobenzene[h]	4.16 ± 0.11 (n = 2)	d

(Continued)

Table 1. (Continued)

CAS No.	Chemical	Log K_{ow}	Source
2524-09-6	0,0,S-triethylester phosphorodithioic acid	3.12	e
66-75-1	Uracil mustard	0.16	e
1330-20-7	Xylene(ortho)	3.12	f

a. Standard deviation
b. Generally, use of K_{ow}s for charged or ionizable species as a predictive sorption parameter is unwarranted (see Results and Discussion).
c. Nitrogen mustard alkylating agents – half-life in water at pH 7 and 25°C is usually less than one day.
d. Measured at ERL-Athens
e. CLOGP
f. Starlist
g. CAS No. refers to Thiodan, a mixture of Endosulfan I and Endosulfan II
h. CAS No. refers to "Trichlorobenzene," K_{ow} of the 1,2,4 isomer was measured.

Table 2. Comparative Log K_{ow} Values

Chemical	CLOP[a]	AERL[b]	Literature[c]
Aldrin	5.09	5.11 ± 0.04[d] (n = 4)	5.52[8]
Azaserine		-2.00 ± 0.06 (n = 3)	-1.08[5]
Biphenyl		4.09 ± 0.12 (n = 8)	3.99 ± 0.12 (n = 5)[4] 3.88[4]
Chlorambucil	3.61	Hydrolysis rate too fast $t_{1/2}$ < 2 hrs at 25°C, pH7	2.74[5]
Chlordane	5.54 (Tech)	6.01 ± 0.30[e] (n = 4) 6.41 ± 0.10[f] (n = 4)	6.00[4] 2.78[5] 5.48[6]
Diallate		4.49 ± 0.06 (n = 4)	0.73[5]

(Continued)

Table 2. (Continued)

Chemical	CLOP[a]	AERL[b]	Literature[c]
Dieldrin		4.09 ± 0.05 (n = 2)	4.34[11]
4,6-dinitro-0-cyclohexyl phenol	3.75	4.12 ± 0.04 (n = 4)	
Endosulfan II		4.52 ± 0.10 (n = 3)	
Endrin	4.32	4.92 ± 0.18 (n = 4)	5.34[9] 5.16[10] 4.56[6]
Ethylene-bis-(dithio-carbamic acid) as disodium salt		-2.70 ± 0.07 (n = 3)	
Heptachlor	4.61	5.53 ± 0.22 (n = 4)	5.44[6] 4.41[8]
Kepone		5.30 ± 0.09 (n = 4)	2.00[5]
Lasiocarpine	0.33	1.28 ± 0.14 (n = 4)	0.99[5]
Pronamide	2.95	3.43 ± 0.10 (n = 4)	
Pyrene	5.05 ± 0.16	5.05 ± 0.27 (n = 13)	5.22 ± 0.05 (n = 2)[4]
Toxaphene	4.02	04.63 ± 0.33 (n = 4)	5.50[2] 2.92[7] 3.30[8]
1,2,4-Trichloro-benzene	4.28	4.16 ± 0.11 (n = 2)	4.06 ± 0.11 (n = 4)[12,13]

a. Calculated using CLOGP
b. Measured at ERL-Athens
c. Superscript numbers identify data sources listed in "References."
d. Standard deviation
e. *cis* isomer of chlordane
f. *trans* isomer of chlordane

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